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## USE OF COLEMANITE FOR IMPROVING THE QUALITY OF UNFRITTED GLAZES

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A thorough investigation of the boron-containing component — colemanite — is performed. Glaze coatings using colemanite are synthesized. The optimal content of colemanite in the batch composition is 3–6%, which makes it possible to expand the interval of glaze formation by lowering the temperature at which the glassy phase appears from 1150 to 1000°C. While retaining the required physical and chemical properties, the synthesized coatings differ by high values of the aesthetic indicators: brightness — 87%, whiteness — 89%.

Improving the quality of coatings for ceramic sanitary ware while at the same time expanding the raw materials base and lowering the cost of raw materials remains a real problem in modern ceramic production. One indicator which needs to be improved is the quality and aesthetic characteristics of opacified glaze coatings, so that specialists are continually searching for effective compositions and components that can improve these characteristics.

The present investigation is devoted to obtaining bright opacified coatings for ceramic sanitary ware fired at high temperature with a natural mineral — colemanite  $\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$  — added as a boron-containing component; the colemanite is provided by the state company Eti Mine Works G.M. (Turkey). This company was created in 1935 and is the largest Turkish company whose business is to obtain and reprocess minerals. The company produces and supplies a number of enriched boron minerals and purified boron products, such as concentrated colemanite, ulexite, tincal, purified sodium tetraborate pentahydrate Étibor-48, sodium tetraborate decahydrate, water-free sodium tetraborate, and boric acid.

Created in 1982 in Finland, the daughter company Ab Etiproducts Oy now has exclusive rights to sell Eti Mine Works G.M. products in Russia and the Commonwealth of Independent States, the Baltic countries, and Scandinavia.

Colemanite is an interesting but still little-studied boron-containing mineral which is virtually unused in the ceramic industry. For this reason, a thorough investigation of colemanite and determination of its effect on the physical–chemical properties of glass-crystalline coatings and their phase composition and aesthetic characteristics are of scientific and practical interest.

Colemanite can be represented by different morphological formations: crystals ranging from short to long columnar modifications and geodes ranging from granular to continuous aggregates with white, gray, or yellowish colors. Colemanite is characterized by a glassy luster, hardness 4.0–4.5, density 2420–4200 kg/m<sup>3</sup>, and perfect cleavage. When heated colemanite dissolves in hydrochloric acid, and it is insoluble in water. Accompanying minerals are gypsum  $\text{CaSO}_4$ , kernite  $\text{Na}_2\text{B}_4\text{O}_6(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ , sodium tetraborate  $4[\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot 8(\text{H}_2\text{O})]$ , and ulexite  $\text{NaCa}(\text{H}_2\text{O})_6[\text{B}_3\text{B}_2\text{O}_7(\text{OH})_4]$ . Colemanite is known as a product of change of pandermite  $\text{Ca}_2(\text{H}_2\text{O})[\text{B}_4\text{BO}_7(\text{OH})_5]$ .

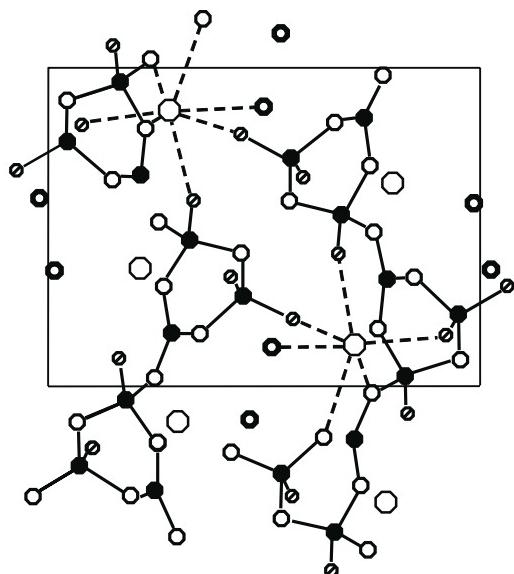
The structure of colemanite (Fig. 1) is represented by infinite chains of  $[\text{BO}_3]$  triangles and  $[\text{BO}_4]$  tetrahedra bound together. The composition of one link of a chain is  $[\text{B}_3\text{O}_4(\text{OH})_4]^{-2}$  and the link consists of two  $[\text{BO}_4]$  tetrahedra and one  $[\text{BO}_3]$  triangle, which are joined at common vertices, forming a closed ring. Calcium atoms and water molecules are present between the chains. Each calcium atom lies at the center of a polyhedron with an irregular shape, formed by four oxygen atoms (or hydroxyl groups) and one water molecule. The calcium atoms bind separate boron–oxygen chains in layers. These atoms, together with hydroxyl groups and water molecules, connect neighboring layers with one another [1].

The colemanite used in our work has the following chemical composition (%<sup>2</sup>): 5.66 SiO<sub>2</sub>, 36.54 B<sub>2</sub>O<sub>3</sub>, 0.35 Al<sub>2</sub>O<sub>3</sub>, 23.49 CaO, 2.61 MgO, 0.30 Na<sub>2</sub>O, and 30.98 other impurities.

Thermogravimetric data (Fig. 2) have shown that the initial material studied undergoes a series of transformations when heated. For example, a stepped endothermal effect with

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<sup>2</sup> Here and below — the mass content.

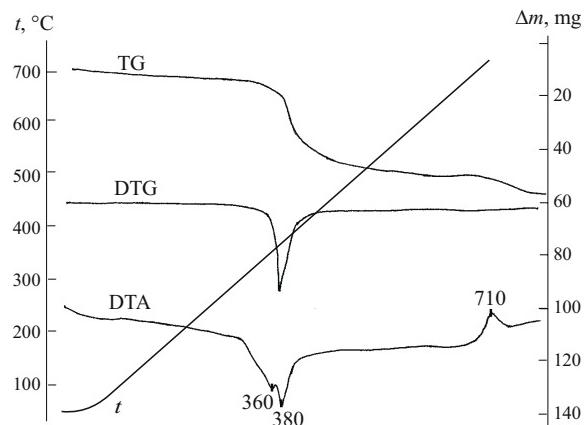


**Fig. 1.** Crystal – chemical structure of colemanite:  $\square$ ) Ca;  $\circ$ ) O;  $\bullet$ ) OH;  $\square$ )  $\text{H}_2\text{O}$ ;  $\blacksquare$ ) B.

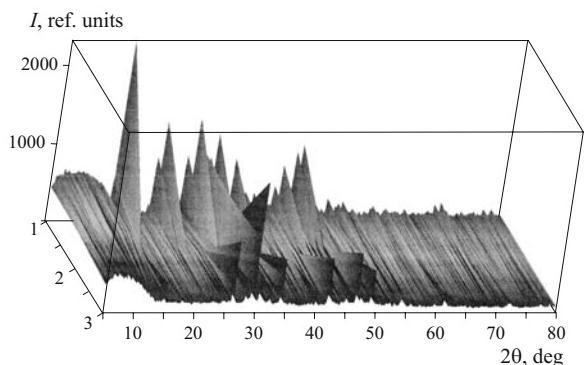
minima at 360 and 380°C is observed in the temperature interval 310 – 420°C. As temperature increases further, an exothermal effect with a maximum at 710°C appears. The total mass loss is 23%.

To determine the nature of the processes occurring, an x-ray analysis was performed of the initial colemanite and the colemanite heat-treated at 400 and 800°C, using a Bruker (Germany) D8 diffractometer. The dynamics of phase transformations of the experimental material on heating is displayed in Fig. 3. The investigations showed that the initial raw material component consists primarily of the mineral colemanite with a negligible amount of calcite  $\text{CaCO}_3$  present. During heat treatment the raw material undergoes a series of transformations: the structure of colemanite is completely destroyed at temperatures 360 and 380°C. This is accompanied by a transition of colemanite into an amorphous state with the initial amount of  $\text{CaCO}_3$  preserved, and an exothermal effect corresponding to the formation of a new crystalline compound — calcium borate — is observed at 710°C.

Boron anhydride  $\text{B}_2\text{O}_3$  is a strong flux. It performs the following functions in glazes: it initiates the formation of melt at the early stages of heat treatment; it decreases the viscosity and surface tension of the glazing glass, thereby promoting rapid curing of the coating and formation of a smooth surface; it decreases the CLTE of the glaze, which is very important in the production of the ceramic sanitary ware manufactured from semiporcelain pastes and, correspondingly, is characterized by comparatively low values of this indicator; it increases the index of refraction and improves the exterior appearance of the glaze; and, it increases the chemical stability [2].



**Fig. 2.** Thermogram of colemanite.



**Fig. 3.** Dynamics of phase transformations of colemanite on heating: 1) initial colemanite; 2, 3) colemanite heat-treated at 400 and 800°C, respectively.

On this basis colemanite as a boron-containing natural material is a very promising component for use in the initial compositions for the production of high-quality glaze coatings.

It should be noted that in the present work we studied the possibility of using, aside from colemanite, a boron-containing component — calcium borate — which is conventionally used in the production of glazes. It was established experimentally that the best coatings are glazes obtained using colemanite. During the preparation of the glaze slip, calcium borate has a negative effect on the rheological properties of the suspension, causing it to cement and to settle, which is inadmissible under production conditions, since it makes it difficult to pour the glaze out of the mill after milling and transporting it along the slip ducts and to deposit it on the intermediate product using robots.

The base composition chosen for the investigations was a composition consisting of unfritted opacified glaze [3], containing Chupitskoe pegmatite, quartz sand, zirconobite, wollastonite concentrate, Belgorod chalk, Vesko-Granitik refractory clay, and Glukhovetskoe kaolin. It should be noted that in our investigations we used, instead of ordinary quartz

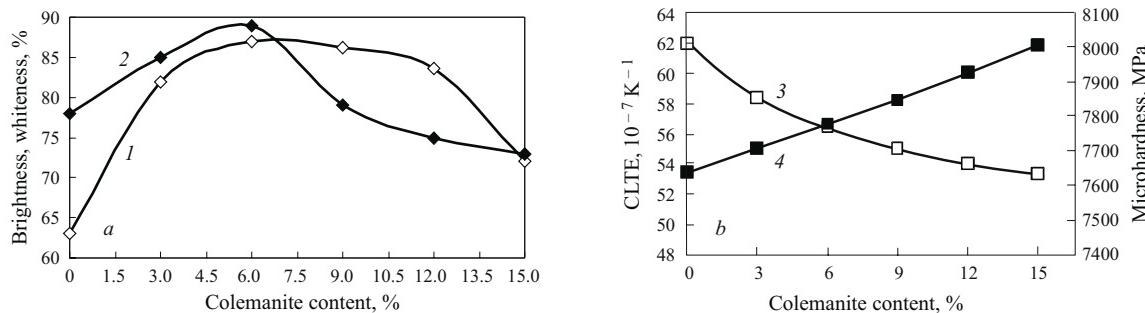


Fig. 4. Decorative – aesthetic characteristics (a) and physical – chemical properties (b) of glaze coatings versus colemanite content in the batch (above 100%): 1) brightness; 2) whiteness; 3) CLTE; 4) microhardness.

sand, milled quartz dust with the following granulometric composition (%): residue on No. 016 sieve — 0.50, No. 010 — 1.25, No. 0063 — 1.92; sieving through a No. 005 sieve — 90.53. This replacement is made because glass formation in unfrittened glazes occurs during calcination, which gives the best homogenization of the glaze melt formed, more complete dissolution of quartz grains during calcination, and correspondingly increases the quality of the coatings produced.

To investigate the influence of colemanite on the properties of glass-crystalline coatings for ceramic sanitary ware, the coatings were synthesized by introducing colemanite into the batch compositions in amounts ranging from 3 to 15% (above 100%) with a 3% step variation.

To obtain the required rheological characteristics of the glaze suspension, sodium tripolyphosphate was introduced into its composition. To obtain a pure white color under artificial illumination, cobalt sulfate was also added to the batch. Sodium tripolyphosphate and cobalt sulfate were added above 100% of the glaze components.

The glaze was prepared by the conventional ceramic technology to milling thinness 0.4 – 0.6% on a No. 0045 sieve followed by deposition of the suspension on intermediate ceramic sanitary ware dried to residual moisture content not exceeding 1%. The glazed samples were calcined for 22 h with holding time 1.5 h at the maximum temperature  $1180 \pm 20^\circ\text{C}$  in a tunnel furnace manufactured by the Sacmi firm of Keramin JSC.

Visual assessment of the samples showed that introducing colemanite greatly decreases the melting temperature of the glaze, which is indicated by the appearance of a glassy phase at lower heat-treatment temperature, equal to approximately  $1000^\circ\text{C}$  as compared to  $1150^\circ\text{C}$  without the use of the indicated component. In addition, a distinct improvement of the pouring of the glaze is observed and the number of defects, mainly pinholes, decreases; removing pinholes is the main and as yet unsolved problem in the production of ceramic sanitary ware. The samples are distinguished by enhanced whiteness, reaching 89%, as a result of not only a high degree of opacification but also the formation of a high-quality surface.

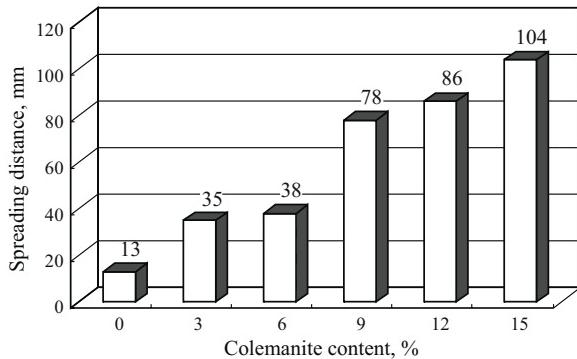
The brightness and whiteness indicators were determined using a BF-2 photoelectric brightness meter. The CLTE of all experimental samples was measured on a DIL 402PC electronic dilatometer (NETZSCH, Germany). The refractive index, whiteness, and CLTE of the coatings versus the quantity of the colemanite and, correspondingly,  $\text{B}_2\text{O}_3$  introduced are shown in Fig. 4.

It was determined that adding up to 6.0% (above 100%) colemanite increases the brightness and whiteness of the coatings. This is explained by the somewhat earlier appearance of a liquid phase and a decrease of its viscosity. The best combination of crystalline and glassy phases of the coatings is obtained for this content of colemanite; the coatings are characterized by adequate opacity and possess a high brightness. Introducing more than 12.0% colemanite causes overfiring of the glazes at calcination temperature  $1200 \pm 20^\circ\text{C}$ , caused by the formation of a lower-melting low-viscosity glassy phase, and decreases the brightness of the coatings substantially.

The CLTE lies in the range  $(53 - 62) \times 10^{-7} \text{ K}^{-1}$ , and decreases as the  $\text{B}_2\text{O}_3$  content increases. The introduction of multiply charged ions, such as boron, with low coordination number with respect to oxygen results in their using the weakly bound to oxygen from alkali-metal oxides to construct their own coordination sphere. As a result, the total strength of the bonds in the glaze increases and, in consequence, the CLTE exhibits a pronounced tendency to decrease.

Analysis of the interrelation of the physical – chemical characteristics of the compositions of the experimental opacified glazes with the addition of colemanite showed that the microhardness of the coatings increases and the CLTE of the coatings decreases as the amount of  $\text{B}_2\text{O}_3$  introduced with colemanite in their composition increases.

Analysis of the properties investigated shows that the highest values of the decorative – aesthetic characteristics (brightness, whiteness) and physical – chemical properties (microhardness, matching of CLTE of the ceramic base and the glaze coating, pouring, coverage) are observed for compositions with 3 – 6% colemanite content.



**Fig. 5.** Glaze spreading distance versus colemanite content in the batch (above 100%).

Determining in the thermal stability of articles is an indirect method for monitoring the matching of the glaze and the ceramic base. It was determined that all glaze coatings which were investigated provide the required thermal stability: after double boiling in a 50% solution of calcium chloride no hairline cracking (spotting), dimpling, or other damage was observed on samples under visual examination.

Investigation of the chemical stability, determined by holding the samples for 1 h in three solutions in parallel (20%  $H_2SO_4$ , 20% HCl, and 5% KOH), showed that the glazes met the standard requirements.

It is well-known that the quality of a coating is largely determined by the melting temperature of the glaze and the viscosity of the glaze melt at the highest calcination temperature, which determines to a large extent the wetting capacity of the coating, and greatly influences the permeation of the melt into the ceramic base. In addition, the viscosity also affects the degree of opacification of the coatings, influencing the formation of crystalline phases [4]. For example, on the one hand, a higher viscosity slows down the formation and growth of crystals, thereby preserving the glassy state of the glaze, while on the other hand low viscosity does not allow adequate crystallization of a coating, since it impedes separation of phases and formation of a micro-heterogeneous structure. Therefore, viscosity is a very important technological parameter, which must be taken into account when synthesizing coatings.

The viscosity was measured indirectly by determining the spreading distance of a glaze melt along an inclined surface of the intermediate product of unglazed porcelain for

sanitary ware. The glaze used at Keramin JSC with spreading distance 35–40 mm served as a standard. The measurements showed (Fig. 5) that for 3 and 6% colemanite content the spreading distance is 35 and 38 mm, respectively; this satisfies the requirements and serves as a criterion for selecting the optimal amount of colemanite in the initial compositions.

X-ray phase analysis showed that the main crystalline opacifying phase in all samples of the coatings investigated is zircon  $ZrSiO_4$ . Wollastonite  $CaSiO_3$  and  $\alpha$ -quartz  $\alpha-SiO_2$  are present in negligible quantities, and the intensity of their diffraction peaks decreases with increasing colemanite content; this can be explained by a decrease of the deformation temperature of the glassy phase and an increase of its amount as a result of an increase in the content of the  $B_2O_3$  entering with colemanite, intensifying the process. The decrease in the intensity of the characteristic peaks of zircon can be explained by the fact that the decrease of the viscosity of the glaze melt formed promotes amorphization of the  $ZrSiO_4$  particles.

In summary, colemanite, which is a natural boron-containing raw-material component, decreases during calcination the viscosity of the glaze melt and expands the interval of glaze formation by decreasing the onset temperature of formation of the liquid phase from 1150 to 1000°C and does not have a negative effect on the rheological properties of the glaze suspension. The decorative – aesthetic characteristics — brightness (87%) and whiteness (89%) — are preserved when the required physical – chemical properties for unfritted opacified glaze coatings for ceramic sanitary ware are maintained.

Factory tests at Keramin JSC showed that colemanite in opacifie, unfritted glazes is promising for ceramic sanitary ware.

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